

FINAL REPORT

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**Au/MnO_x Catalytic Performance Characteristics
for Low-Temperature CO Oxidation**

**Effect of CO₂ on the Performance of
Au/MnO_x and Pt/SnO_x Low-Temperature
CO Oxidation Catalysts**

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ABSTRACT

Manganese oxide-supported gold (Au/MnO_x) catalysts have been prepared and tested for low-temperature (< 100°C) CO oxidation in stoichiometric mixtures of CO and O₂ containing no CO₂ in the feed gas. Even with no pretreatment these catalysts are superior to the best, pretreated platinized tin oxide (Pt/SnO_x) catalysts under the conditions tested. The very small decay observed for Au/MnO_x catalysts is mostly due to CO₂ retention. The optimum Au content has been determined to be 10 at% of the Mn content, and a Li promotor results in improved catalytic behavior over K- or Na-promoted Au/MnO_x catalysts for the conditions examined in this study.

INTRODUCTION

The development of low-temperature CO oxidation catalysts has become an important research topic during the last ten years due to the many potential areas of application. These include air-purification devices for respiratory protection, pollution control devices for reducing industrial and automatic emissions, and CO₂ lasers that require recombination of CO and O₂ produced in the laser to maintain high power output. CO gas sensors also are based on catalytic materials used for CO oxidation.

Many different catalysts have been prepared and tested for low-temperature CO oxidation activity. Stark and coworkers (1-3) were the first to report that platinized tin oxide (Pt/SnO_x) is an effective catalyst for this reaction. Haruta and coworkers (4-6) screened a number of reducible-oxide supported metals and found that gold supported on iron oxide (Au/ α -Fe₂O₃) and cobalt oxide (Au/Co₃O₄) are also efficient CO oxidation catalysts, while Gardner and coworkers performed a similar type of screening and found that gold supported on manganese oxide (Au/MnO_x) is highly efficient (7). Haruta and coworkers (6,8-10) and Lin et al. (11) have also found that Au supported on titania is active for CO oxidation. During the last ten years, efforts have been made to optimize the Pt/SnO_x catalyst (12,13), and other groups have described other catalysts (12) that are less active than those discussed above. Hoflund and coworkers have carried out surface characterization studies using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and ion scattering spectroscopy (ISS) on various Pt/SnO_x catalysts (13-15), the Au/MnO_x catalyst (16) and Au/ α -Fe₂O₃ and Au/Co₃O₄ catalysts (17). These studies provide compositional and chemical-state information on these various catalysts. Reductive pretreatment has a significant effect on the chemical behavior of the Pt/SnO_x catalysts. This has been examined in previous characterization studies (13-15, 18). The mechanism of CO oxidation at low temperatures is fairly well understood for Pt/SnO_x catalysts (19), but considerably less is understood about Au/MnO_x catalysts.

In a comparison of the performance characteristics of Pt/SnO_x and Au/MnO_x catalysts (20), Au/MnO_x catalysts were shown to be superior to Pt/SnO_x catalysts when the feed gas

contains no CO_2 . An improved Pt/SnO_x catalyst has been formulated by supporting a thin layer of Pt/SnO_x on silica. The purpose of this present study is to present further comparison of the Au/MnO_x catalyst with the silica-supported Pt/SnO_x catalyst and to present information on the Au/MnO_x catalyst regarding the effects of Au loading, pretreatment, alkali promoters and support on a cordierite monolith.

EXPERIMENTAL

Catalyst Preparation

The Au/MnO_x sample was prepared by coprecipitation from aqueous tetrachloroauric acid, manganese (II) nitrate, and sodium carbonate. Lithium carbonate and potassium carbonate were used instead of sodium carbonate to produce the Li-promoted and K-promoted Au/MnO_x catalysts respectively. The precipitate was washed with hot water, dried in air at 110°C and calcined in air at 400°C for 4 h. The Au/MnO_x composition is based on the molar ratio of Au:Mn in the precursor solutions. The BET surface area of the Au/MnO_x catalysts is about $60 \text{ m}^2/\text{g}$.

A 10% Au/MnO_x catalyst dispersed on a cordierite monolith was prepared by a coprecipitation technique using HAuCl_4 , $\text{Mn}(\text{NO}_3)_2$ and Na_2CO_3 . A $1'' \times 3'' \times 1/2''$ section of monolith with 400 cells/in² (Dow Corning Industries) was immersed in a solution of Na_2CO_3 and deaerated under vacuum for 1 h. Then the monolith was transferred to the coprecipitation vessel where it was suspended in a fresh solution of Na_2CO_3 . HAuCl_4 and $\text{Mn}(\text{NO}_3)_2$ were added slowly with constant stirring for about 45 min until coprecipitation was complete. The coated monolith was removed and washed twice with hot (90°C) deionized water and then dried in air at 110°C for 24 h before calcining in air at 400°C for 4 h. The total weight of the prepared monolith was 9.452 g and 0.100 g was Au/MnO_x . The initial surface area was $1 \text{ m}^2/\text{g}$.

For the Pt/SnO_x catalysts the SnO_x support was prepared by dissolving Sn powder in nitric acid and heating to dryness at 150°C . This process was carried out in the presence of deaerated SiO_2 particles in order to produce silica-supported Pt/SnO_x . Pt deposition was

accomplished by reducing tetraaminoplatinum (II) hydroxide with formic acid in the presence of the deaerated SnO_x or $\text{SnO}_x/\text{SiO}_2$ supports. The resulting slurry was dried in air at 150°C . The BET surface areas of the Pt/SnO_x catalysts is about $130\text{ m}^2/\text{g}$.

Reactor Studies

Unless stated otherwise, the reactor studies were performed by placing 50 mg of powdered catalyst in a quartz tubular reactor and flowing 10 sccm of the reaction gas mixture consisting of 1 vol% CO, 0.5 vol% O_2 and 2 vol% Ne in He (no CO_2) at a total pressure of 1 atm through the catalyst. The Ne was included as the calibration standard for the gas chromatograph (GC) used to monitor the reaction products. The procedure for starting the reaction varied depending upon whether the catalyst was pretreated. The nonpretreated samples were exposed to 10 sccm of He for 1 h as the reactor temperature stabilized at either 35 or 55°C . Pretreated samples were heated to the desired pretreatment temperature in 10 sccm of He for 1 h, exposed to 10 sccm of the pretreatment gas for 2 h, and cooled to the reaction temperature in 10 sccm of He for 1 h. In both cases the He flow was subsequently replaced with the reaction gas and product sampling was initiated. At predetermined time intervals an automated sampling valve directed a 1-ml portion of the reaction products to the GC for quantitative determination of the moles of CO_2 formed per second-gram of catalyst, and these results were plotted versus time to yield the CO oxidation activity curves shown in the figures.

RESULTS AND DISCUSSION

A comparison of the activities of 15% Au/MnO_x , 14.5% $\text{Pt}/\text{SnO}_x/\text{SiO}_2$ and 19.5% Pt/SnO_2 for CO oxidation at 35 and 55°C is presented in figure 1. None of these catalysts were pretreated before running the reaction. This is particularly important in applications where pretreatment is not possible or where the catalysts must be stored in or exposed to air before use. The catalytic behavior of the Au/MnO_x catalyst is clearly superior to the Pt/SnO_x catalysts under the conditions used in this experiment. Not only is the activity of the Au/MnO_x catalyst greater,

but its activity apparently does not decay. In fact, the Au/MnO_x activity is increasing slowly with time at both 35 and 55°C. Pretreatment of the Pt/SnO_x catalysts increases their activities. A comparison between the activities of 10% Au/MnO_x and pretreated 14.5% Pt/SnO_x/SiO₂ is shown in figure 4 of the previous study (20). The activity of the Pt/SnO_x catalyst is higher after pretreatment, but the activity decay is still large and there is a 10-day period of instability during which time the activity decreases and then increases. This behavior has been attributed to changes in the surface moisture content of the Pt/SnO_x catalysts (18). The Au/MnO_x catalysts do not exhibit this type of initial behavior. Their activities usually increase monotonically rapidly at first and then slowly over the time periods examined. In some cases they slowly decrease monotonically or go through a small maximum in activity before decreasing slowly.

Under the reaction conditions selected for these tests, the reactor is an integral reactor because the conversion is larger than a few percent. CO oxidation is highly exothermic, and its rate is strongly dependent upon the reaction temperature as observed in figure 1. Reaction conditions including sample size, flow rate, feed composition and the He carrier gas have all been selected in order to minimize the surface heating effect so that accurate activity data could be obtained at a given temperature. Different conditions have been used in all of the various studies of low-temperature CO-oxidation catalysts, and these conditions significantly affect the results so it is inappropriate to compare the activity data from different studies. Direct comparative studies of Au/MnO_x, Au/α-Fe₂O₃ and Au/Co₃O₄ catalysts are in progress (21). Furthermore, studies have not yet been carried out to determine the rate expression and activation energy for CO oxidation over Au/MnO_x catalysts.

The effects of a 125°C pretreatment in He on two different preparations of 5% Au/MnO_x catalysts are shown in figure 2. There is a significant variation in the activities of these two catalysts even though they were prepared from the same chemicals using the same prescription two days apart. This activity difference is larger than that normally observed, but the reason for this is not understood. For the more active catalyst, the pretreatment essentially has no effect, but the pretreatment improves the performance of the less-active catalyst. This type of

pretreatment is reductive and may cause a change in chemical state of the surface species. Also, species such as H_2O and CO_2 would desorb under these conditions. Any of these changes may be responsible for the performance increase of the less-active catalyst. In the previous study (20) it was found that a 50°C pretreatment for 2 hours in 5 vol% CO in He results in a 15% improvement of activity. A similar pretreatment at higher temperatures does not result in a further improvement, and a mild pretreatment in an oxidizing environment results in poorer performance.

The effect of increasing Au content on the CO oxidation activity of Au/MnO_x catalysts is shown in figure 3. The activity of MnO_x is quite low, and the addition of 2% Au increases its activity by a factor of 10. Since Au does not catalyze this reaction below 100°C and the MnO_x support has a very low activity, there is a synergistic interaction between the Au and MnO_x support that is responsible for the high catalytic CO oxidation activity at these low temperatures. The surface characterization study (16) and a transmission electron microscopy study (21) of these catalysts suggest that most of the Au is in nonmetallic form, which is consistent with the above statement that metallic Au is not active for this reaction under these conditions. The Au is highly dispersed on the MnO_x and probably interacts strongly with the support. Increasing amounts of Au to 10% result in increased activity, but larger amounts decrease the catalytic activity as observed in figure 3. Haruta and coworkers (6,9,10) believe that very small Au crystallites are responsible for the catalytic activity of supported Au catalysts toward CO oxidation. The data shown in figure 3 are consistent with this assertion. At low Au content the dispersion is high and the activity increases as the Au content increases. However, at higher Au content the dispersion decreases as larger crystallites form, and the activity decreases as observed. The reaction data obtained from the better 5% Au/MnO_x catalyst and shown in figure 2 exhibits initial activities which are similar to those obtained from 10% Au/MnO_x catalysts. However, its decay rate is much larger so it is inferior to the 10% Au/MnO_x catalyst.

Each of the Au-containing catalysts was outgassed briefly by switching from the reaction gas mixture to pure He. During this outgassing, CO_2 detected by the GC desorbs from the

catalyst surface. When the reactor feed is switched back to the reaction gas mixture, the catalyst activity is increased as observed in figure 3. Several conclusions can be drawn from these data. Firstly, CO₂ retention is a process that causes activity decay of these catalysts. Secondly, the rate of decay correlates with the magnitude of the activity increase after outgassing; i.e., catalysts with larger decay rates outgas more CO₂ and exhibit larger increases in activity. This trend is apparent in figure 2. The 10% Au/MnO_x catalyst exhibits the lowest decay rate and the lowest activity increase whereas the 2% Au/MnO_x catalyst exhibits the largest decay and the largest increase in activity after the outgassing. Thirdly, the decay for Pt/SnO_x catalysts (figure 1) are quite large as are their increases in activity after outgassing (22). Therefore, Au/MnO_x catalysts are less susceptible to CO₂ poisoning than Pt/SnO_x catalysts under the conditions examined in this and the previous studies (20,22). CO₂ retention is not the only process responsible for the activity decay of low-temperature CO oxidation catalysts. Other processes include change of the surface moisture content, poisoning by a component in the feed gas, chemical-state changes at the catalyst surface and morphological changes. The effects of these processes can often be reversed by giving the catalyst another pretreatment.

The first Au/MnO_x catalysts were prepared using a sodium carbonate solution (7), and ISS data collected from these samples (16) exhibit a large Na peak. Alkali-metal ions including Li⁺, Na⁺, Rb⁺, K⁺ and Cs⁺ are often used as promoters in partial and complete oxidation catalysts. Based on these considerations Li-promoted and K-promoted 2% Au/MnO_x were prepared using Li₂CO₃ and K₂CO₃ instead of Na₂CO₃ for comparison with the Na-promoted 2% Au/MnO_x catalyst. The results are shown in figure 4. The Li-promoted 2% Au/MnO_x catalyst exhibits the best performance over the period tested, but the K-promoted 2% Au/MnO_x catalyst is also significantly better than the Na-promoted 2% Au/MnO_x catalyst. Since an alkali metal carbonate is required in the preparation, it is not possible to prepare a nonpromoted Au/MnO_x catalyst. Outgassing experiments may provide evidence that the presence of the alkali metal ion may suppress CO₂ retention. The decay of Au/MnO_x catalysts prepared with different alkali metals has not been studied yet.

For most applications the catalyst must be supported on a porous material such as alumina in pellet or honeycomb form so that it can easily be incorporated into the catalyst bed. In this study 2.460 g of 10% Au/MnO_x supported on cordierite was tested. Of this 0.026 g was 10% Au/MnO_x, and the total surface area was about 2.5 m². The comparable values for the 10% Au/MnO_x powder catalyst was 0.050 g of Au/MnO_x and about 3 m² of total surface area. The activity curve obtained from the cordierite-supported 10% Au/MnO_x catalyst at 35, 55 and 100°C is shown in figure 5. The activities at 35 and 55°C are quite low, and temperatures as high as 100°C are required to achieve a conversion similar to that of the powder catalyst under the conditions tested. This may partially be due to flow considerations but probably results mostly from a low catalytically active surface area due to agglomeration of the Au/MnO_x on the support. Haruta et al. (23) have prepared an Au/α-Fe₂O₃ catalyst on a porous alumina support, and they also find that higher temperatures are required to yield significant conversions. Further study will most likely lead to improved alumina-supported Au/MnO_x catalysts.

SUMMARY

Various Au/MnO_x catalysts have been prepared and tested for low-temperature CO oxidation in stoichiometric mixtures of CO and O₂ containing no CO₂. Even with no pretreatment Au/MnO_x catalysts are superior to Pt/SnO_x catalysts with regard to both activity and decay under the conditions tested. The optimum Au content is 10 at% of the Mn content. Outgassing experiments indicate that CO₂ retention is a process which contributes to their fairly small but observable decay rate. Au/MnO_x catalysts with lower or higher than optimum Au contents exhibit larger decay rates that correlate with increased CO₂ retention. Na-, Li- and K-promoted Au/MnO_x catalysts have been prepared and tested. Significant differences are observed with the Li promotor providing the best performance under the conditions examined. A supported Au/MnO_x catalyst has been prepared on a cordierite honeycomb monolith. This catalyst exhibits lower activity than the powder catalyst which may be due to poor dispersion of the Au/MnO_x on the alumina support.

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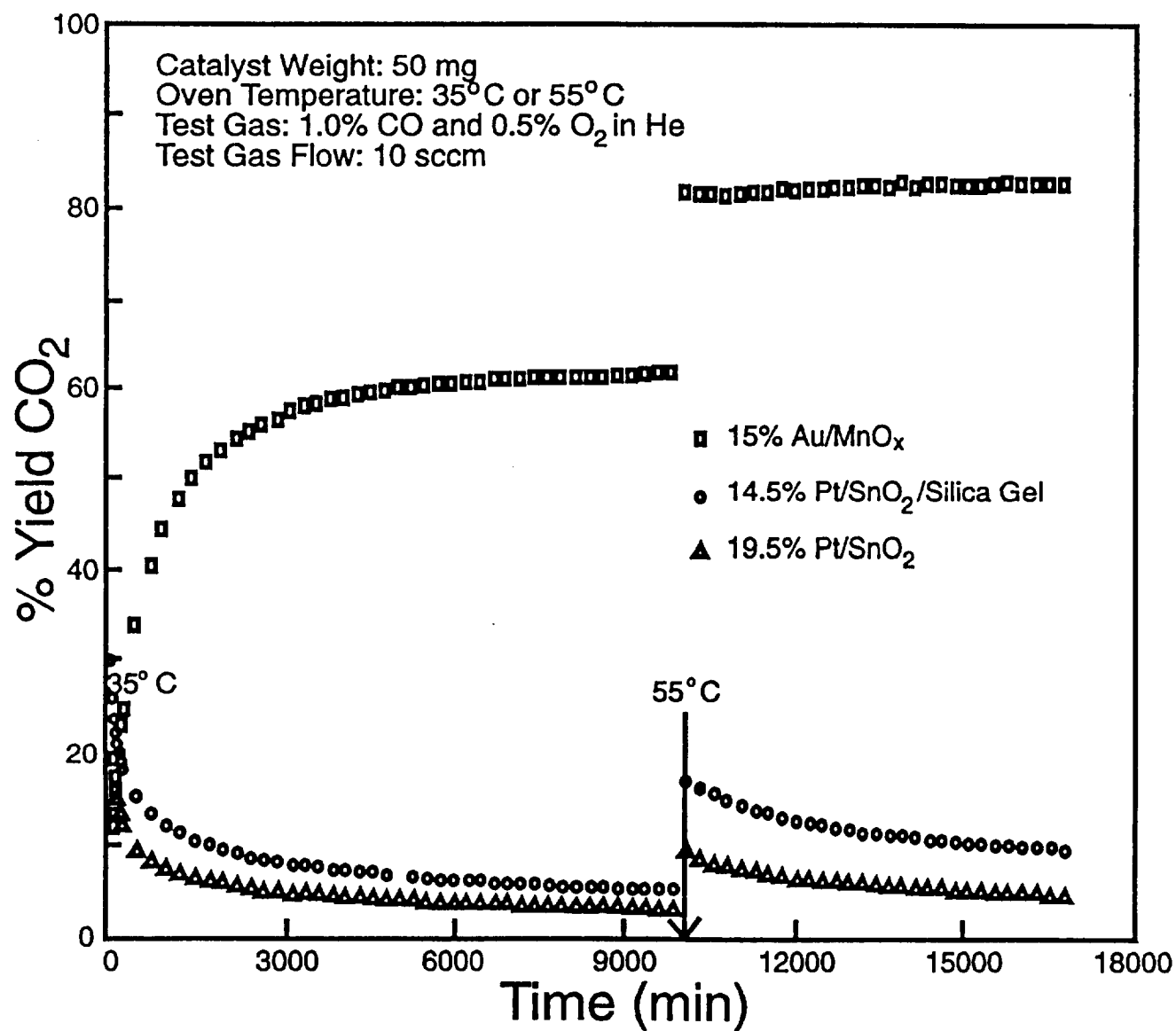
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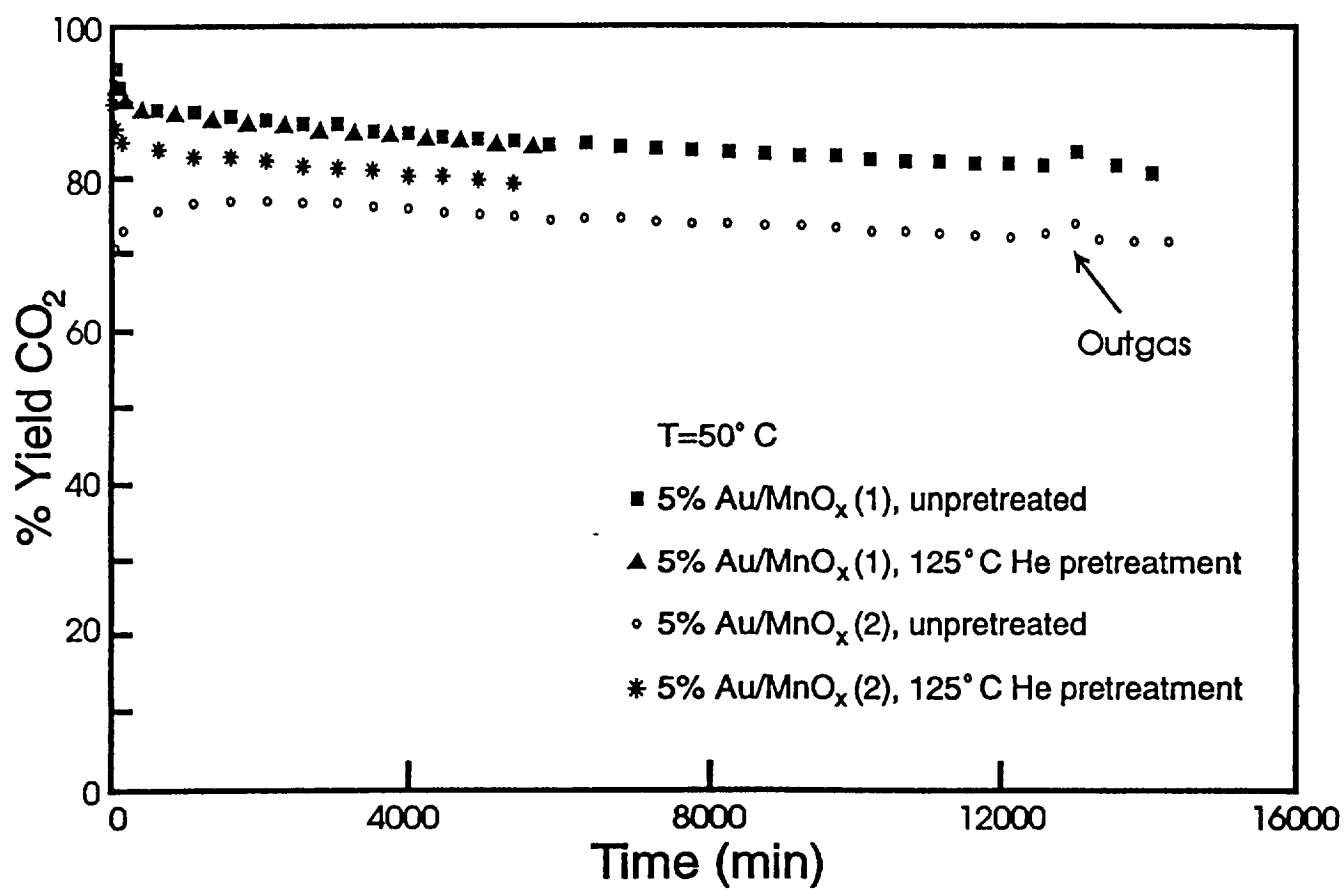
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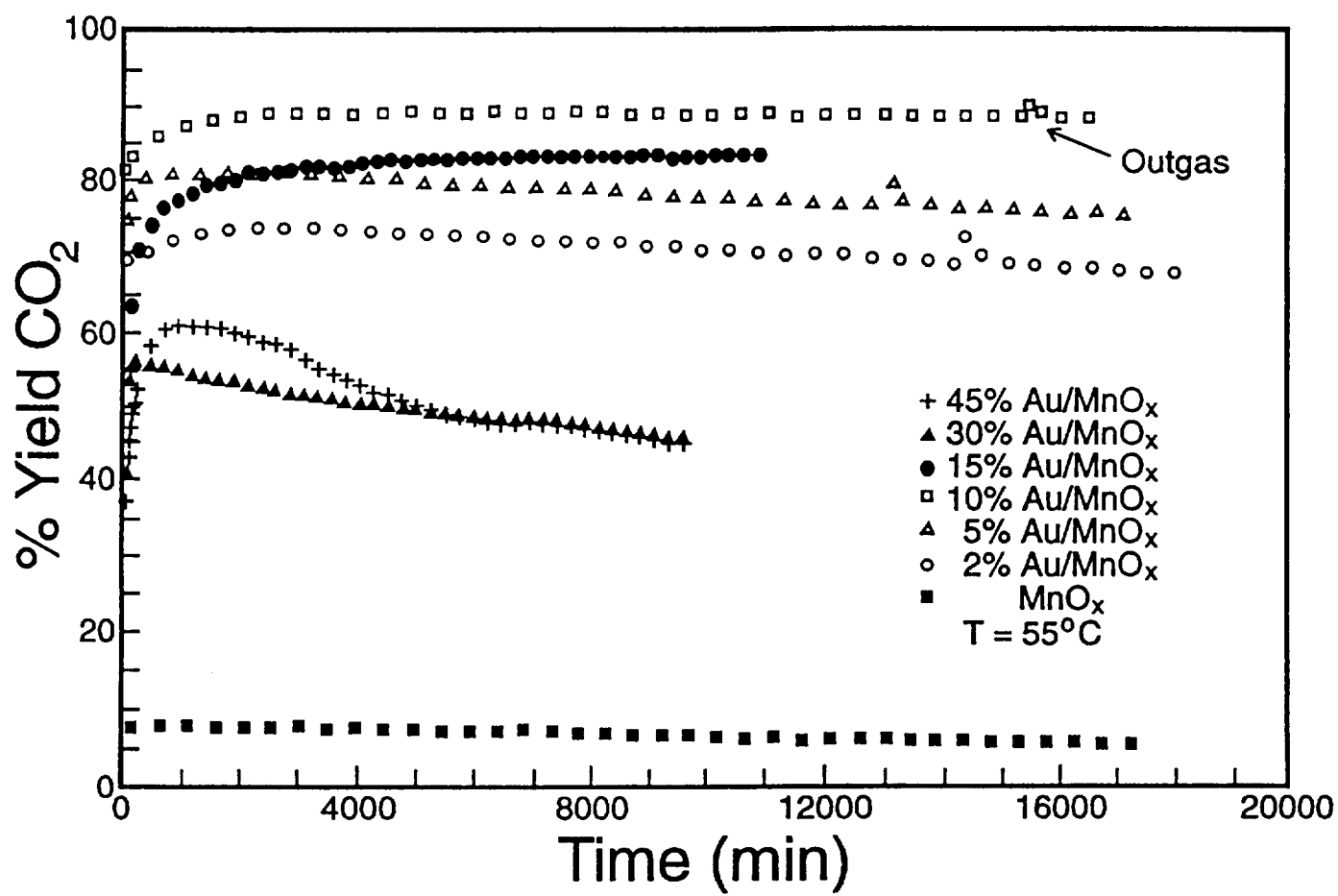
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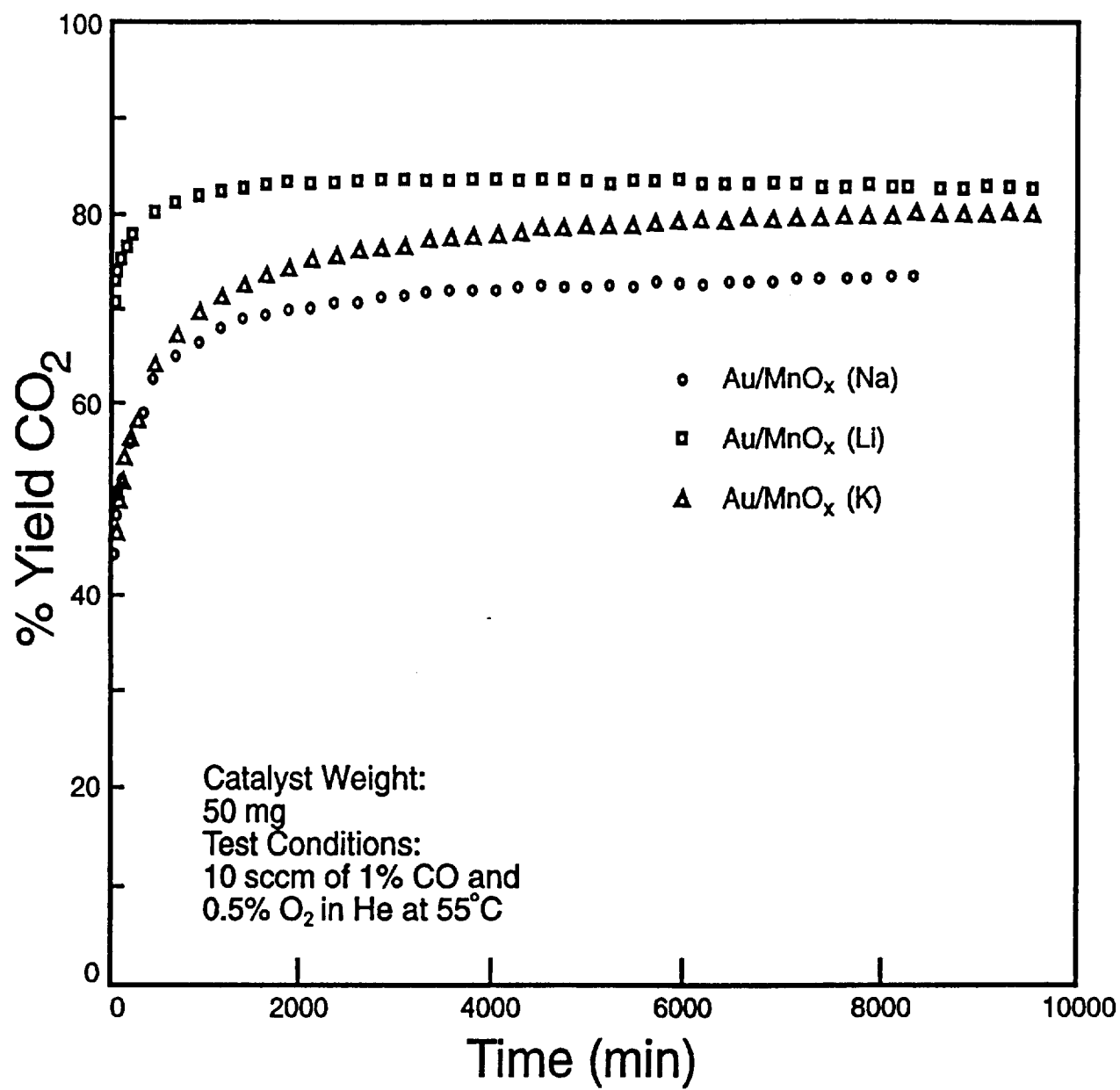
FIGURE CAPTIONS

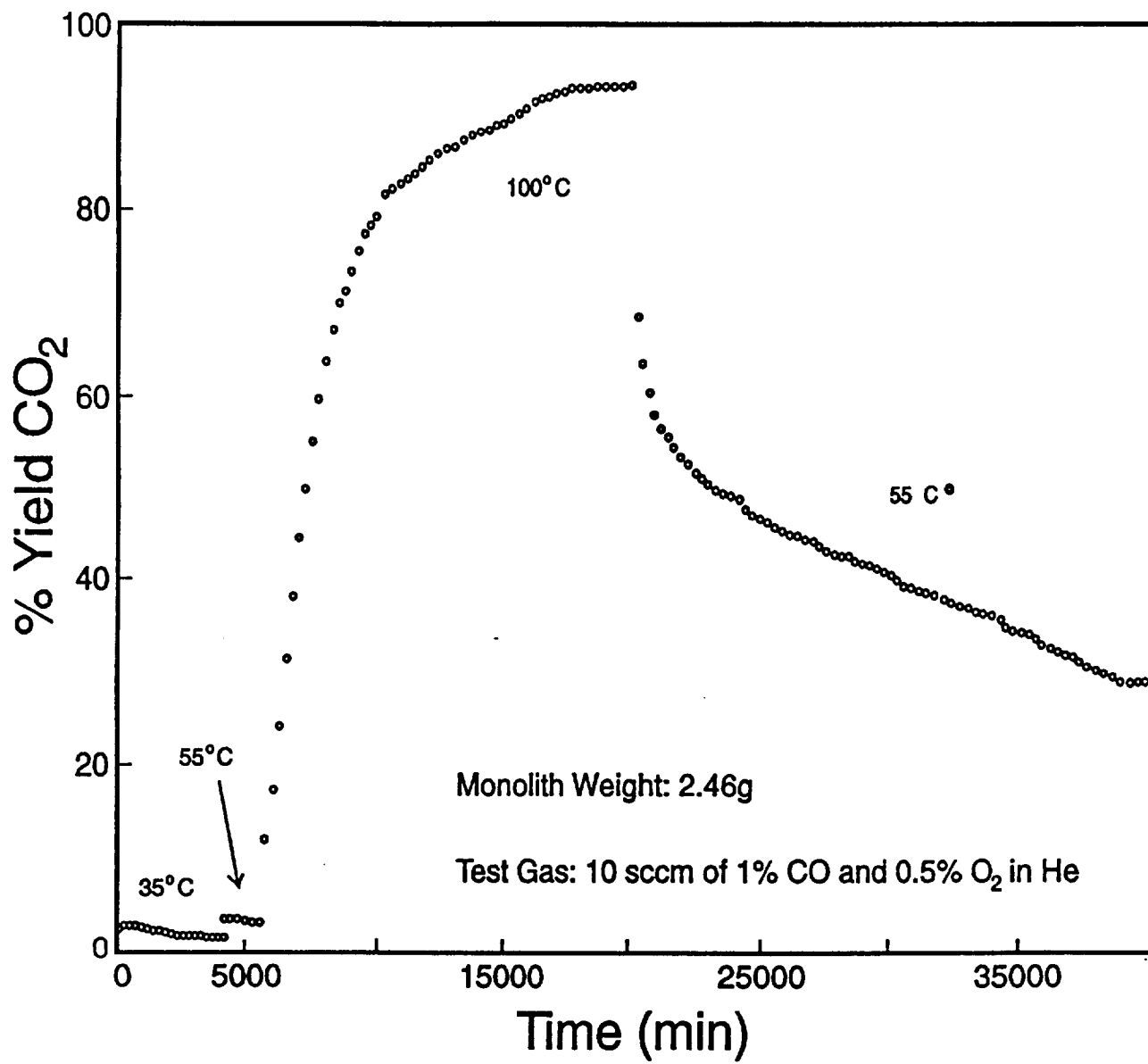
- Figure 1 Activity curves for 15% Au/MnO_x, 14.5% Pt/SnO_x/SiO₂ and 19.5% Pt/SnO_x. None of these catalysts were pretreated. The temperature was raised from 35 to 55°C after a period of 10,000 min.
- Figure 2 Effect of a 125°C pretreatment in He on the activity of two different 5% Au/MnO_x catalysts.
- Figure 3 Effect of varying Au content and outgassing on the CO oxidation activity of Au/MnO_x catalysts. The reaction gas mixture consisted of 1% CO and 0.5% O₂ in He at a flow rate of 10 sccm and temperature of 55°C.
- Figure 4 Comparison of Li-, K- and Na-promoted 2% Au/MnO_x catalysts.
- Figure 5 Activity curve for 10% Au/MnO_x supported on a cordierite monolith. The total weight is 2.46 g, the Au/MnO_x weight is 0.026 g, and the total surface area is 2.5 m².











ABSTRACT

The performance of Au/MnO_x and Pt/SnO_x catalysts for low-temperature (< 100°C) CO oxidation under stoichiometric conditions has been examined for the case where 8 or 16% CO₂ is added to the feed gas. High concentrations of CO₂ in the reaction gas mixture adversely affect the behavior of these catalysts due to CO₂ retention at their surfaces. The magnitude of this detrimental effect can be reduced by adding an Fe promotor to both types of catalysts and optimizing various preparative and pretreatment variables.

INTRODUCTION

Efforts to develop efficient low-temperature ($< 100^{\circ}\text{C}$) CO oxidation catalysts began over ten years ago when Stark and coworkers (1-3) demonstrated that platinized tin oxide is effective for this function. Their primary interest was to develop a catalyst for use in closed-cycle CO_2 lasers (4,5) in order to maintain a high power output. O_2 formed by decomposing CO_2 in the laser electrode region results in rapid power loss. This problem can be overcome by catalytically combining the stoichiometric amounts of CO and O_2 formed in the discharge. Since then, other applications relating to air pollution control and use as sensor materials have become important.

Many catalysts have been screened over the last seven years (5-13) in order to identify new catalysts for low-temperature CO oxidation. A number of catalysts have been identified which may be classified as noble metals on reducible oxides (NMRO catalysts (5)). There are many variables involved in the preparation, pretreatment and reaction which all significantly affect the catalytic activity and decay behavior of the different catalysts. In an effort to understand the behavior of these catalysts, characterization studies using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and ion scattering spectroscopy (ISS) have been carried out by Hoflund and coworkers on Pt/SnO_x catalysts (14-16), Au/MnO_x catalysts (17) and $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$ and $\text{Au/Co}_3\text{O}_4$ catalysts (18).

The catalytic activity data presented in studies of these catalysts (4-8,19-21) have been obtained using reactor feed mixtures containing only low concentrations of the reactants CO and O_2 usually in the stoichiometric ratio (4,5,8,19-21) or O_2 rich (6,7). However, recently presented reaction data on Pt/SnO_x and Au/MnO_x catalysts (19,20) demonstrate that CO_2 retention is a primary factor contributing to decay of their activities and that Pt/SnO_x catalysts typically are affected more severely than Au/MnO_x catalysts. These results suggest that the presence of significant amounts of CO_2 in the feed gas may result in poisoning of these catalysts. Since the CO_2 concentration level is quite large in CO_2 lasers (typically 8 to 16%), it is necessary to examine the influence of high CO_2 concentrations on the behavior of Pt/SnO_x and Au/MnO_x catalysts.

CO oxidation over Pt metal occurs by a Langmuir-Hinshelwood mechanism between adsorbed O and adsorbed CO to form CO₂ which rapidly desorbs. Although CO₂ does not inhibit this reaction, CO does act as inhibitor at low temperatures < 200°C because CO completely covers the surface making it impossible for the dissociative adsorption of O₂. Above this temperature some CO desorbs allowing O₂ to adsorb resulting in the catalytic oxidation of CO. Clearly, the low-temperature catalytic oxidation (< 100°C) of CO does not proceed by this mechanism. Schryer et al. (22) have proposed a two-site mechanism for low-temperature CO oxidation over prerduced Pt/SnO_x catalysts in which an O adsorbed on a reduced Sn site couples with CO adsorbed on Pt and a surface hydroxyl group to form a surface bicarbonate species which decomposes to yield CO₂. An alternate pathway is proposed through formation of a surface formate species which decomposes to yield CO₂. Both pathways are possible, and experimental evidence suggests that both are involved in the catalytic reaction (5). For either pathway retention of CO₂ leads to increased coverage of the surface by the intermediate species and decay of the catalytic activity. Furthermore, higher CO₂ partial pressures above these catalysts may shift the equilibrium toward retention of CO₂.

EXPERIMENTAL

Catalyst Preparation

Several different Au/MnO_x and Pt/SnO_x catalysts were prepared and examined in this study in order to determine how certain preparation variables alter catalytic behavior.

Au/MnO_x Catalysts

The Au/MnO_x catalysts were prepared by coprecipitation at 70°C from aqueous tetrachloroauric acid, manganese (II) nitrate, and sodium carbonate. A solution of HAuCl₄ (5.31 g in 1000 ml of water) and a solution of Mn(NO₃)₂ (35 g in 1000 ml of water) were added dropwise over a 2 h period to 1.2 l of a 0.5 M Na₂CO₃ solution at room temperature while stirring. For preparation of some of the catalysts, lithium carbonate was used instead of sodium

carbonate because Li has been shown to be a more effective promotor than Na under stoichiometric reaction conditions without added CO_2 (20). The precipitate was washed twice with hot water, dried in air at 110°C for 18 h and calcined in air at 300 or 400°C for 4 h. Fe-promoted Au/MnO_x catalysts were prepared by adding iron (III) nitrate to the solution containing the Au and Mn. The resulting composition is based on the atomic ratio of Fe:Mn:Au in the precursor solution. The BET surface areas of these catalysts are about $60 \text{ m}^2/\text{g}$ of catalyst (19), and the chemical composition of the near-surface region has been discussed previously (17).

Pt/SnO_x Catalysts

Pt/SnO_x catalysts were prepared by dissolving Sn powder in nitric acid and heating the mixture to dryness at 150°C . Pt deposition was accomplished by reducing tetraaminoplatinum (II) hydroxide with formic acid in the presence of the deaerated SnO_x support. Drying was accomplished by heating in air at 150°C for 4 h. The Pt concentration based solely on the Pt and Sn content is 19.5% for the Pt/SnO_x catalyst examined in this study. A silica-supported Pt/SnO_x catalyst was also prepared and examined in this study. To prepare this catalyst, silica powder was added to the nitric acid. Then 30-mesh metallic Sn granules were added, and the resulting slurry was dried in air at 150°C . The drying was done slowly over a 14 h period. Based on ion scattering spectroscopy (ISS) data, the tin oxide film completely coats the silica surface (15). This material was impregnated, as described above, to yield a Pt content of 15% (referred to as the 15% Pt/SnO_x/SiO₂ catalyst). An Fe promotor was incorporated into this catalyst by adding $\text{Fe}(\text{NO}_3)_3$ to the impregnating solution such that it was 1 at% of the Pt plus Sn content. A total mass of 250 g of this catalyst contains 200 g of silica. The BET surface areas of these Pt/SnO_x catalysts is about $130 \text{ m}^2/\text{g}$ of catalyst. The composition and chemical state distribution of nonpromoted Pt/SnO_x/SiO₂ catalysts have been examined using ISS and XPS before and after reductive pretreatments (15).

Reactor Experiments

The catalytic reaction was carried out in a tubular reactor at 35 or 55°C using 50 mg of Au/MnO_x catalysts or 19.5% Pt/SnO_x and 250 mg (including 200 mg of silica) of the silica-supported Pt/SnO_x catalyst. The reaction gas mixture consisted of 1% CO, 0.5% O₂ and 0, 8 or 16% CO₂ in He at a flow rate of 10 sccm and 1 atm total pressure. The reaction feed gas also contained 2% Ne as a calibration standard for the gas chromatograph (GC) used to monitor the products. The experimental procedure was varied depending upon the catalyst pretreatment. He-pretreated catalysts were exposed to 10 sccm of He for 1 h as the reactor temperature stabilized. Reductively pretreated catalysts were heated in 10 sccm of pure He as the reactor temperature stabilized at 125°C, exposed to 10 sccm of the pretreatment gas (5 vol% CO in He) for 1 h at 125°C and cooled to the reaction temperature in 10 sccm of He for 1 h. The reaction was begun by switching flow to the reaction mixture at which time product sampling was initiated. The space velocities were 26.7 s⁻¹ for the Au/MnO_x and Pt/SnO_x catalysts and 5.3 s⁻¹ for the Pt/SnO_x/SiO₂ catalysts. Since the space velocities, the weights used and the surface areas of the Au/MnO_x and Pt/SnO_x/SiO₂ catalysts were all different, it is not possible to make direct comparisons of the activities of these two types of catalysts. The differences in the factors between the two catalysts cause the activities of the Pt/SnO_x/SiO₂ catalysts to be larger than those of the Au/MnO_x catalysts. If all factors were similar, the Au/MnO_x catalysts would be more active than the Pt/SnO_x/SiO₂ catalysts.

RESULTS AND DISCUSSION

The effect of the presence of 16% CO₂ in the reaction gas mixture on the catalytic behavior of 10% Au/MnO_x catalysts (He-pretreated) is shown in figure 1. The three sets of data shown in figure 1 were collected simultaneously in three different quartz reactor tubes. Two different catalyst batches prepared three weeks apart were used. Both batches were run with no CO₂ in the feed, and one was run with 16% CO₂ in the feed. The two different samples run with no CO₂ in the feed exhibit essentially identical catalytic behavior. However, the presence of

CO₂ has a large detrimental effect on the catalytic performance. The catalytic activity is reduced by more than a factor of 2. The activity of the Au/MnO_x catalyst increases over the time period examined when CO₂ is not added to the feed gas, but the reason for this increase is not understood. It probably is related to chemical-state changes of surface species or to changes in the surface moisture or hydroxyl group content. With CO₂ present the activity decays in a normal manner.

At just over 11,000 min, the feed stream was switched from the reaction mixture to pure He for about 2 hours. During that period, CO₂, detected by the GC, outgassed from the catalyst. Upon readmission of the reaction feed gas, the catalytic activity is significantly increased but decays rapidly. The extent of the activity increase correlates with the amount of CO₂ outgassed (not shown) and, hence, provides a measure of the importance of CO₂ retention on decay. The activity increase is small when no CO₂ is present in the feed gas and large when CO₂ is present. This is consistent with the decreased activity and increased decay rate, and these facts indicate that CO₂ retention is enhanced by the addition of CO₂ to the feed gas. Even when no CO₂ is added to the feed, about 0.75 mole % is produced as a product.

A 225°C outgas was carried out at 13,000 min. The resulting activity increases are correspondingly larger than those observed after the 55°C outgas, and the activity increase is very large for the case with CO₂ added to the feed gas. In this case the activity of the catalyst approaches that of the catalysts run without CO₂ added to the feed gas. After the reintroduction of the reaction feed gas, the activities decay rapidly to a fairly steady-state value in both cases. This value is lower than the activity before the 225°C outgas for no added CO₂ and much higher when 16% CO₂ is added to the feed gas. In fact, it is larger than the activities exhibited at any point prior to the outgas. The 55°C outgas does not produce this effect indicating that substantial and complex chemical-state and compositional changes occur during the 225°C outgas. A power failure occurred between 14,300 and 17,000 min. During this time, the reaction continued but activity measurements did not. Upon resumption of the measurements, it is apparent that the activity recovers after the 225°C outgas and continues along its previous path for the case

without CO₂ in the feed gas. The temporary drop in activity may be due to loss of surface moisture during the 225°C treatment which is then replenished with continuing reaction. For the case with 16% CO₂ in the feed gas, the activity remains above that observed before the 225°C treatment but decays steadily at a slightly higher rate. The data shown in figure 1 demonstrate that an increased CO₂ partial pressure results in CO₂ retention at the surface which produces a decay in catalytic activity.

The catalytic behavior of two pretreated Pt/SnO_x catalysts and 10% Au/MnO_x catalysts with and without a pretreatment is shown in figure 2 for a feed gas containing 8% CO₂ at a reaction temperature of 55°C. 50 mg of the 10% Au/MnO_x and the 19.5% Pt/SnO_x catalysts were used while 250 mg of the Pt/SnO_x/SiO₂ catalyst was used because the 200 mg of silica was not included in the catalyst weight. Clearly, if the silica were included, the Au/MnO_x catalysts would be superior to the Pt/SnO_x catalysts in the presence of CO₂ as they are without CO₂ added to the feed gas (23). A reductive pretreatment significantly lowers the activity of the 10% Au/MnO_x catalyst. The best performance is achieved by using Au/MnO_x catalysts after calcining and storing in air. This is an advantage of Au/MnO_x catalysts over Pt/SnO_x catalysts particularly in applications where it is not possible to pretreat the catalyst. Since the CO₂ concentration is 8% in this case compared to 16% for the data shown in figure 1, the activity of the nonpretreated Au/MnO_x catalyst is higher in figure 2. For example, at 10,000 min the activity is at a 45% conversion level in figure 2 and about 30% in figure 1. As discussed in another study (16) and observed in figure 2, the addition of Fe to Pt/SnO_x catalysts results in high catalytic activity and an activity decay rate similar to those of the other catalysts.

Further activity data obtained from Au/MnO_x and Pt/SnO_x catalysts are shown in figure 3. The CO₂ concentration in the reaction gas was 8%, and the temperature was 35°C. In this case the catalytic behavior of two Fe-promoted Au/MnO_x catalysts containing different amounts of Fe, a nonpromoted Au/MnO_x catalyst and the Fe-promoted Pt/SnO_x/SiO₂ catalyst are shown before and after various treatments. During the first 5,000 min, the catalysts tested were not pretreated. Without a pretreatment the activity of the Fe-promoted Pt/SnO_x/SiO₂ catalyst is low

as expected (14). The Fe-promoted Au/MnO_x catalyst with an atomic ratio of 0.1 Fe:1 Mn:0.1 Au exhibits a significantly higher activity than Au/MnO_x, but the Fe-promoted Au/MnO_x catalyst with a larger Fe content (atomic ratio of 1 Fe:1 Mn:0.2 Au) exhibits a lower activity. Therefore, a certain amount of Fe is beneficial but a larger amount degrades the catalytic performance of Au/MnO_x catalysts. A similar behavior has been found for Fe-promoted Pt/SnO_x/SiO₂ catalysts (21). The activity decay rates are high, and it appears that the decay rate decreases as Fe content increases.

Then the catalysts were pretreated for 1 h and the reaction runs were continued for three of the catalysts. The pretreated, Fe-promoted Pt/SnO_x/SiO₂ catalyst exhibits the typical initial dip in activity before entering a more gradual activity decay. The precise nature of this dip in activity is not known, but Schryer et al. (24) have shown that it is related to surface moisture content. When water is added to the feed gas, the dip is not present in the activity versus time data. The activity of the Fe-promoted Pt/SnO_x/SiO₂ catalyst is very high after the pretreatment, but it also exhibits a very high decay rate. Consistent with the data shown in figure 2, reductive pretreatment leads to loss in activity of the Au/MnO_x catalysts (23). After 5000 min both the active Fe-promoted and nonpromoted Au/MnO_x catalysts exhibit quite similar behavior so the beneficial effect of the Fe is lost by reductive pretreatment.

At 10,000 min the catalysts were exposed to air at 35°C for 1 hour. The activities of both the Au/MnO_x and Fe-promoted Pt/SnO_x/SiO₂ catalysts are increased by this treatment due to outgassing of CO₂. The activity increase of the Fe-promoted Pt/SnO_x/SiO₂ is much larger than those of the Au/MnO_x catalysts indicating that CO₂ retention is more severe for the Fe-promoted Pt/SnO_x/SiO₂ catalyst. This is consistent with the fact that the activity decay rate is also much larger for the Fe-promoted Pt/SnO_x catalyst. The large activity decay of the Fe-promoted Pt/SnO_x/SiO₂ catalyst indicate that significant chemical change occurs at this surface. Previous surface characterization studies of Pt/SnO_x model surfaces and catalysts have shown that a Pt/Sn alloy forms during the reductive pretreatment (14,15,25,26) and that this alloy is destroyed during air exposure by formation of a tin oxide overlayer on a Pt-rich region (27,28). This

indicates that air exposure of the Fe-promoted Pt/SnO_x/SiO₂ catalyst results in migration of Sn to the surface where it is oxidized and covers the Pt causing a loss of surface Pt and a faster decay due to CO₂ retention. After air exposure the activities of both Au/MnO_x catalysts proceed along paths similar to those expected had the catalysts not been exposed to air indicating that surface compositional and chemical-state changes caused by the air exposure are negligible.

At 20,000 min the catalysts were subjected to an air exposure for 50 hours at 35°C. The resulting activity increase is very large for the Fe-promoted Pt/SnO_x/SiO₂ catalyst. The activity decay exhibited by this catalyst is larger than that observed after the 1-hour air exposure suggesting the possibility that the same chemical changes occur but to a greater extent. Interesting behavior is observed for both Au/MnO_x catalysts after the 50-hour air exposure. The activities are increased significantly, and the decays are altered. The activity curves exhibit small dips followed by increases in activity. The magnitude of the activity increase and the decay characteristics suggest that the detrimental effects of the reductive pretreatment are reversed for the Au/MnO_x catalysts by the 50-hour air exposure.

The effects of varying Au loading, calcining temperature, and the use of Li₂CO₃ rather than Na₂CO₃ on the catalytic behavior of Fe-promoted Au/MnO_x catalysts have been examined, and the results are shown in figures 4 and 5. Two preparations of Fe-promoted 10% Au/MnO_x catalysts were prepared using Li₂CO₃ and Na₂CO₃. Each preparation was split into three portions. One portion was just dried in air at 110°C, another was calcined at 300°C, and the third portion was calcined at 400°C. The catalytic behaviors obtained in the resulting six runs are shown in figure 4. Data obtained using a nonpromoted 10% Au/MnO_x catalyst prepared using Li₂CO₃ and calcined at 300°C are also shown. The catalysts prepared using Na₂CO₃ exhibit higher activities than those prepared using Li₂CO₃. There is also a consistent trend within each set of preparations regarding calcining temperature. The catalyst calcined at 300°C is the most active, and the catalyst calcined at 400°C is the least active. Three different catalysts with varying Au content were prepared: Fe/Mn/Au atomic ratios of 0.1/1/0.1, 0.1/1/0.15 and 0.1/1/0.2. According to the data shown in figure 5, the Fe-promoted 10% Au/MnO_x catalyst is

the most active. A similar conclusion was reached in comparing the activities of nonpromoted Au/MnO_x catalysts without CO₂ added to the reaction gas mixture by examining catalysts with 0, 2, 5, 10 and 15% Au (19).

SUMMARY

Various preparations of Au/MnO_x and Pt/SnO_x catalysts have been examined for low-temperature CO oxidation activity under stoichiometric conditions in the presence of 8 or 16 at% CO₂ added to the reaction gas mixture. The increased CO₂ partial pressure has a large detrimental effect on the performance of these catalysts. It lowers their catalytic activity due to CO₂ retention and increases their decay rates. Utilization of an Fe promotor in both Au/MnO_x and Pt/SnO_x catalysts improves their performance in the presence of CO₂. A reductive pretreatment lowers the performance of Au/MnO_x catalysts but enhances the performance of Pt/SnO_x catalysts. During a catalytic run, exposure of the catalyst to an inert gas or air results in outgassing of CO₂ from the catalyst. After this treatment the catalytic activity is increased and the extent of the activity increase provides a measure of the CO₂ retention. Furthermore, a change in the decay rate indicates alteration of the surface during the treatment. The effects of varying preparation and pretreatment variables on the catalytic properties of Au/MnO_x catalysts have been examined. For the values of the variables tested under the reaction conditions of this study, the best Au/MnO_x catalyst is: nonpretreated, Fe promoted with an Au/Mn/Fe ratio of 0.1/1/0.1, prepared using Na₂CO₃ and calcined at 300°C.

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FIGURE CAPTIONS

- Figure 1 Effect of CO₂ on the catalytic behavior of 10% Au/MnO_x catalysts.
- Figure 2 Comparison of the catalytic behavior of the 19.5% Pt/SnO_x catalyst (50 mg), the silica-supported Pt/SnO_x catalyst (250 mg including 200 mg of the silica support) and the 10% Au/MnO_x catalyst (50 mg) with and without pretreatment. The Pt/SnO_x catalysts were both given reductive pretreatments, and the Au/MnO_x catalyst was pretreated in He only or in He and CO.
- Figure 3 Comparison of the catalytic behavior of two Fe-promoted Au/MnO_x catalysts, an Fe-promoted Pt/SnO_x/SiO₂ catalyst and a nonpromoted Au/MnO_x catalyst with 8% CO₂ added to the reaction gas mixture at a temperature of 35°C. 50 mg of the Au/MnO_x catalysts were used, and 250 mg of the Fe-promoted Pt/SnO_x/SiO₂ catalyst (including 200 mg of SiO₂) was used. The following treatments were performed at the times indicated: (1) pretreatment in 10 sccm of 5% CO in He at 125°C for 60 min, (2) exposure to air at 35°C for 60 min, and (3) exposure to air at 35°C for 3000 min.
- Figure 4 Catalytic behavior of Fe-promoted Au/MnO_x catalysts prepared using Li₂CO₃ or Na₂CO₃ and calcined at different temperatures. The atomic Fe:Mn:Au ratio for these catalysts is 0.1:1:0.1. Data obtained from the nonpromoted 10% Au/MnO_x catalyst are shown for comparison.
- Figure 5 Effect of Au loading on Fe-promoted Au/MnO_x catalysts. The Fe:Mn:Au atomic ratio is 0.1:1:x where x is 0.10, 0.15 and 0.20, the catalysts were calcined at 300°C, and Li₂CO₃ was used in the preparation.

